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(54) **Storable water-silica suspensions for use in well cements**

(57) Water-silica suspensions for use in well cements comprise as, a suspending agent, a colloidal material, clay or a gel-forming polymer, to prevent or reduce settling of the silica during storage.

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Description

[0001] The present invention relates to storable water-silica suspensions for use in well cements.

[0002] Hydraulic cement compositions are commonly utilized in subterranean well completion and remedial opera-

5 tions. For example, hydraulic cement compositions are used in primary cementing operations whereby strings of pipe such as casings and liners are cemented in well bores. In performing primary cementing, a hydraulic cement composition is pumped into the annular space between the walls of a well bore and the exterior surfaces of a pipe string disposed therein. The cement composition is permitted to set in the annular space thereby forming an annular sheath 10 of hardened substantially impermeable cement therein. The cement sheath physically supports and positions the pipe string in the well bore and bonds the exterior surfaces of the pipe to the walls of the well bore whereby the undesirable migration of fluids between zones or formations penetrated by the well bore is prevented.

[0003] When temperatures in the well bore exceed about 230°F (110°C, silica has heretofore been included in the cement composition to prevent cement strength retrogression whereby the strength of the set cement composition decreases and the permeability of the set cement increases. As a result of such strength retrogression, pressurized 15 formation fluids can enter the well bore which is highly disadvantageous.

[0004] The degradation of Portland and the equivalent set cement compositions first occurs in the range of from about 210°F to about 230°F (99°C to 110°C). This degradation has heretofore been prevented by the addition of crystalline silica such as fine silica flour to the cement composition which forms tobermorite gel in the cement composition. The tobermorite is stable up to a temperature in the range of from about 300°F to about 330°F (149°C to 166°C).

20 To maintain the strength of the cement composition above about 300°F (149°C, crystalline silicas such as silica flour or a mixture of silica flour and sand must be present to form truscottolite or xontolite gel in the cement which prevents strength retrogression. Thus, fine silica flour, silica flour, sand, and a mixture of silica flour and sand depending upon the temperature encountered by the cement composition have heretofore been used to prevent strength retrogression of set cement compositions.

25 [0005] Suspensions of fine silica flour, silica flour, sand and mixtures of silica flour and sand in water have been used heretofore in well cements to prevent set cement strength retrogression particularly on off-shore platforms. The water-silica suspensions are convenient for transferring the silica into a cement composition. That is, the water-silica suspensions can be added to a cement composition mixing water thereby avoiding silica dust which if inhaled is detrimental 30 to human health. The water-silica suspensions can be prepared on shore and shipped to well locations in containers or drums. However, the watersilica suspensions used heretofore settle and separate over time, and as a result, agitating equipment during storage of the suspensions must be utilized to prevent such settling and the formation of hard cake in the bottoms of containers.

35 [0006] Thus, there are needs for improved water-silica suspensions which are highly resistant to settling and which after being stored can simply and easily be stirred and poured prior to use.

[0007] We have now found a way in which this can be achieved.

[0008] In one aspect, the present invention provides a storable water-silica suspension for use in well cement compositions, which suspension comprises: water; silica; and a suspending agent selected from colloidal materials, clays and gel forming polymers.

40 [0009] The invention also includes a method of cementing a well bore, which method comprises combining a suspension of the invention, with a cement composition comprising a hydraulic cement and water; introducing the mixture into a well bore; and allowing it to set.

[0010] As mentioned above, silica is commonly blended with cement which produces silica dust hazardous to personnel, particularly on off-shore platforms. To avoid this hazard, silica has heretofore been added to water on shore and the suspension formed has been shipped to the well location in tanks or drums where they are stored and added 45 to well cement compositions when needed. However, such water-silica suspensions have heretofore suffered from the disadvantage that they develop free water, settle over time and produce hard cake during storage, all of which require agitation equipment to prevent. The present invention provides stabilized water-silica suspensions which are highly resistant to settling whereby the suspensions can be stored for long periods of time without agitation.

50 [0011] A storable water-silica suspension for use in well cement compositions of this invention is basically comprised of water, silica and an effective amount of a suspending agent selected from microfine particulate colloidal materials, clays and gel forming polymers.

[0012] The water utilized to form a storable water-silica suspension of this invention can be fresh water or salt water. The term "salt water" is used herein to mean unsaturated salt solutions and saturated salt solutions including brine and seawater. Generally, water from any source can be utilized so long as the water does not react with silica or other 55 components in cement compositions to which the water-silica suspensions are added.

[0013] The silica utilized in the water-silica suspensions of this invention can be fine silica flour, silica flour, sand or mixtures thereof. Fine silica flour is crystalline silica and has a particle size smaller than 20 microns. Silica flour is crystalline silica which is produced by grinding sand. The particle size of silica flour is generally in the range of from

about 20 to about 40 microns. Sand is also crystalline silica and the sand can have a particle size in the range of from about 80 to about 500 microns.

[0014] As mentioned, silica is included in well cement compositions to prevent strength retrogression when the well exceeds about 230°F. Set cement composition strength retrogression occurs at temperatures which cause the initially formed reaction products in the cement composition to be converted to secondary reaction products. The conversion causes the set cement composition to decrease in compressive strength and to increase in permeability. Both the decrease in compressive strength and the increase in permeability are detrimental to the function of the set composition, i.e., centering the pipe string in the well bore and preventing pressurized formation fluids from entering the well bore. There are two high temperature ranges where cement strength retrogression can occur. The first is a temperature range of from about 210°F to about 230°F. When the set cement composition reaches that range, the calcium silicate hydrate gel in the cement reacts to alpha calcium silicate hydrate which causes degradation of the cement. This initial degradation is prevented by the addition of either amorphous or crystalline silica to the cement composition so that when the composition sets, tobermorite is formed which does not degrade until a temperature range of from about 300 to about 320°F (149°C to 160°C) is reached. That is, when about 300°F is reached, the cement composition again degrades unless crystalline silica has been added to the cement composition which forms a stable reaction product upon setting, i.e., truscottolite or xontolite. Thus, if a cement composition will reach a temperature range of from about 210°F to about 230°F, the degradation of the set cement can be avoided by including crystalline silica such as fine silica flour, silica flour or mixtures thereof in the cement composition. Fly ash and ground blast furnace slag are amorphous silica sources that can also be used to prevent strength retrogression to at least 300°F. If the cement composition will reach the higher temperature range of from about 300°F to about 330°F, crystalline silica must be added to the cement composition to prevent degradation, i.e., silica flour, sand or mixtures thereof must be added to the cement composition. Generally, in order to prevent the degradation caused by set cement strength retrogression, water suspensions containing fine silica flour, silica flour, sand or mixtures thereof must be included in cement compositions.

[0015] The silica utilized in a water-silica suspension of this invention is present therein in a general amount in the range of from about 50% to about 250% by weight of the water in the suspension, preferably in an amount in the range of from about 150% to about 233% and more preferably in an amount of about 175%.

[0016] The suspending agent in the water-silica suspension functions to prevent water separation and settling in the suspension during its storage. In accordance with the present invention the suspending agent is selected from fine particulate materials, (less than 1 micron) hereinafter referred to as colloidal materials, clays and gel forming polymers. Examples of colloidal materials which can be used include, but are not limited to, carbon black, lignite, brown coal, humic acid, styrene-butadiene rubber latexes, polyvinyl alcohol latexes, acetate latexes, acrylate latexes, precipitated silica and pyrogenic silica (such as an oxidation product of SiO₂, SiH₄, SiC₁₄ or HsiC₁₃). Of these, carbon black is presently preferred. The clays which can be utilized include, but are not limited to, bentonite, attapulgite, kalonite, meta kalonite, hectorite and sepiolite. Of these, bentonite is preferred. The polymers which can be used include, but are not limited to, a copolymer of 2acrylamido-2-methylpropane sulfonic acid and N,N-dimethylacrylamide, carragenan, scleroglucan, xanthan gum, guar gum, hydroxyethylcellulose, carboxymethylhydroxyethylcellulose, hydroxypropylguar, welan gum, acrylic acid copolymers and terpolymers and vinyl acetate copolymers and terpolymers. Of these, a copolymer of 2-acrylamido-2-methylpropane sulfonic acid and N,N-dimethylacrylamide is preferred.

[0017] One or more of the above described suspending agents are generally included in a water-silica suspension of this invention in an amount in the range of from about 0.1% to about 100% by weight of the water in the suspension. When the suspending agent is a colloidal material as described above, the colloidal material in powder form is preferably included in the water-silica suspension in an amount in the range of from about 5% to about 50% by weight of water therein, more preferably in an amount of about 30%. When the suspending agent is a clay as described above, the clay is preferably included in the water-silica suspension in an amount in the range of from about 0.5% to about 8% by weight of water in the suspension, more preferably in an amount of about 5%. When the suspending agent is a polymer described above, the polymer is preferably included in the water-silica suspension in an amount in the range of from about 0.1% to about 3% by weight of water therein, more preferably in an amount of about 1%.

[0018] The methods of cementing a well bore of the present invention are basically comprised of the following steps. A water-silica suspension for preventing cement strength retrogression comprised of water, silica and an effective amount of a suspending agent selected from the group of colloidal materials, clays and gel forming polymers is stored. Thereafter, the water-silica suspension is combined with a cement composition comprised of a hydraulic cement and water. The cement composition including the water-silica suspension is introduced into a well bore and the cement composition is allowed to set therein.

[0019] The hydraulic cements utilized in the cement composition can be those comprised of calcium, aluminum, silicon, oxygen and/or sulfur which set and harden by reaction with water. Such hydraulic cements include Portland cements, pozzolana cements, gypsum cements, high aluminum content cements, silica cements, high alkalinity cements and slag cements. The cements can be of conventional particle sizes or they can be of ultra-fine particle sizes. Portland cements are generally preferred for use in accordance with this invention. Portland cements of the types

defined and described in API Specification For Material And Testing For Well Cements, API Specification 10, 5th Edition, dated July 1, 1990 of the American Petroleum Institute are particularly suitable. Preferred such API Portland cements include classes A, B, C, G and H, with API classes G and H being more preferred and class G being the most preferred. The water utilized in the cement composition can be fresh water or salt water. As mentioned above, the term "salt water" is used herein to mean unsaturated salt solutions and saturated salt solutions including brines and seawater. The water is generally present in the cement composition in an amount sufficient to form a pumpable slurry, generally an amount in the range of from about 38% to about 56% by weight of cement in the slurry. The components of the water-silica suspension utilized in accordance with the methods of this invention are the same as those described above and are utilized in the same amounts set forth above.

5 **[0020]** A preferred storable water-silica suspension of this invention for use in well cement compositions comprises: water; silica selected from the group consisting of fine silica flour, silica flour, sand and mixtures thereof present in the suspension in an amount in the range of from about 100% to about 250% by weight of water therein; and a colloidal suspending agent selected from the group consisting of carbon black, lignite, brown coal, humic acid, styrene-butadiene rubber latexes, polyvinyl alcohol latexes, acetate latexes, acrylate latexes, precipitate silica and pyrogenic silica present in the suspension in an amount of from about 25% to about 100% by weight of water therein.

10 **[0021]** Another preferred storable water-silica suspension of this invention for use in well cement compositions comprises: water; silica selected from the group consisting of fine silica flour, silica flour, sand and mixtures thereof present in the suspension in an amount in the range of from about 50% to about 250% by weight of water therein; and a clay suspending agent selected from the group consisting of bentonite, attapulgite, kalomite, meta kalomite, hectorite and sepiolite, present in the suspension in an amount in the range of from about 0.5% to about 8% by weight of water therein.

15 **[0022]** Yet another preferred storable water-silica suspension for use in well cement compositions of this invention comprises: water; silica selected from the group consisting of fine silica flour, silica flour, sand and mixtures thereof present in the suspension in an amount in the range of from about 50% to about 250% by weight of water therein; and a polymer suspending agent selected from the group consisting of a copolymer of 2-acrylamido-2methylpropane sulfonic acid and N,N-dimethylacrylamide, carragenan, scleroglucan, xanthan gum, guar gum, hydroxyethylcellulose, carboxymethylhydroxyethylcellulose, hydroxypropylguar, welan gum, acrylic acid copolymers and terpolymers and vinyl acetate copolymers and terpolymers present in the suspension in an amount in the range of from about 0.1% to about 3.0% by weight of water therein.

20 **[0023]** A preferred method of cementing a well bore of this invention comprises the steps of (a) storing a water-silica suspension for preventing cement strength retrogression comprised of water, silica selected from the group consisting of fine silica flour, silica flour, sand and mixtures thereof present in the suspension in an amount in the range of from about 50% to about 250% by weight of water therein and a colloidal suspending agent selected from the group consisting of carbon black, lignite, brown coal, humic acid, styrene-butadiene rubber latexes, polyvinyl alcohol latexes, acetate latexes, acrylate latexes, precipitate silica and pyrogenic silica present in the suspension in an amount in the range of from about 25% to about 100% by weight of water therein; (b) combining the water-silica suspension with a cement composition comprised of a hydraulic cement and water; (c) introducing the cement composition including the water-silica suspension into the well bore; and (d) allowing the cement composition to set. The most preferred colloidal suspending agent for use in the above described method is carbon black.

25 **[0024]** Another method of cementing a well bore of the present invention comprises the steps of (a) storing a water-silica suspension for preventing cement strength retrogression comprised of water, silica selected from the group consisting of fine silica flour, silica flour, sand and mixtures thereof present in the suspension in an amount in the range of from about 50% to about 250% by weight of water therein and a clay suspending agent selected from the group consisting of bentonite, attapulgite, kalomite, meta kalomite, hectorite and sepiolite present in the suspension in an amount in the range of from about 0.5% to about 8% by weight of water therein; (b) combining the water-silica suspension with a cement composition comprised of a hydraulic cement and water; (c) introducing the cement composition including the water-silica suspension into the well bore; and (d) allowing the cement composition to set. The most preferred clay suspending agent for use in the above described method is bentonite.

30 **[0025]** Yet another method of cementing in a well bore in accordance with the present invention comprises the steps of. (a) storing a water-silica suspension for preventing cement strength retrogression comprised of water, silica selected from the group consisting of fine silica flour, silica flour, sand and mixtures thereof present in the suspension in an amount in the range of from about 50% to about 250% by weight of water therein and a polymer suspending agent selected from the group consisting of a copolymer of 2-acrylamido-2methylpropane sulfonic acid and N,N-dimethylacrylamide, carragenan, scleroglucan, xanthan gum, guar gum, hydroxyethylcellulose, carboxymethylhydroxyethylcellulose, hydroxypropylguar, welan gum, acrylic acid copolymers and terpolymers and vinyl acetate copolymers and terpolymers present in the suspension in an amount in the range of from about 0.1% to about 3% by weight of water therein; (b) combining the water-silica suspension with a cement composition comprised of a hydraulic cement and water; (c) introducing the cement composition including the water-silica suspension into the well bore; and (d) allowing the cement composition to set. The most preferred polymer suspending agent for use in the above described method

is a copolymer of 2-acrylamido-2methylpropane sulfonic acid and N,N-dimethylacrylamide.

[0026] In order to further illustrate the storable water-silica suspensions and methods of cementing in a well bore in accordance with the present invention, the following example is given.

5 EXAMPLE

[0027] Silica flour was suspended in fresh water containing colloidal carbon black in an amount of 177% silica flour by weight of water in the resulting suspension. The colloidal carbon black suspending agent was present in the suspension in an amount of about 40% by weight of water in the resulting suspension. The suspension identified as Sample 10 No. 1 was stored and monitored over a period of 6 weeks. That is, the sample was examined for free water, settling, whether it was gelled and whether it was re-storable to its original consistency after 3 days, after 1 week, after 3 weeks, and after 6 weeks. The results of these tests are given in the Table below.

[0028] In Sample No. 2, silica flour was suspended in fresh water containing prehydrated bentonite suspending agent in an amount to produce a suspension containing 150% silica flour by weight of water in the suspension. The bentonite 15 suspending agent was present in the suspension in an amount of 5% by weight of water in the suspension. The suspension was stored and the stability of the suspension was monitored after 3 days, after 3 weeks and after 6 weeks. The results of these tests are also given in the Table below.

[0029] Additional Samples Nos. 3, 4 and 5 were prepared by suspending silica flour and/or silica sand in solutions 20 containing a carragenan polymer or copolymer of 2-acrylamido-2methylpropane sulfonic acid and N,N-dimethylacrylamide having a molecular weight of 500.000 to 2.000.000 dalton. Sample No. 3 contained 100% silica flour by weight of water in the suspension and 50% silica sand by weight of water in the suspension and a carragenan polymer suspending agent in an amount of 0.5% by weight of water in the suspension. Sample No. 3 was stored and monitored after 3 days, after 3 weeks and after 6 weeks. The results of these tests are also given in the Table below. Sample No. 25 4 contained only silica flour in an amount of 150% by weight of water in the suspension and a copolymer of 2acrylamido-2-methylpropane sulfonic acid and N,N-dimethylacrylamide in an amount of 0.01% by weight of water in the suspension. Sample No. 5 contained silica sand in an amount of 226% by weight of water in the suspension and carragenan polymer in an amount of 0.5% by weight of water in the suspension. Samples Nos. 4 and 5 were stored and monitored after 3 days and after 3 weeks. The results of these tests are also given in the Table below. In addition, the densities of Samples 30 Nos. 1 through 5 were calculated and the Fann dial readings of the samples after preparation were determined which are given in the Table below.

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TABLE

Test Sample Components, Properties And Stability	Sample No.				5
	1	2	3	4	
<u>Water</u>					
Carbon Black, % by wt. of water in the suspension	40	-	-	-	-
Bentonite, % by wt. of water in the suspension	-	5.0	-	-	-
Carrageenan, % by wt. of water in the suspension	-	-	0.5	-	0.5
Copolymer ¹ , % by wt. of water in the suspension	-	-	-	0.01	-
Silica Flour, % by wt. of water in the suspension	177	150	100	150	-
Silica Sand, % by wt. of water in the suspension	-	-	50	-	226
Density ² , lb./gal.	1.66	1.62	1.61	1.66	1.75
Farm Dial Readings at Rheology, 300-200-100-6-3 rpm	141-112-80-32-29	116-86-57-10-8	160-134-101-45-42	300-1-283-200-12-11	262-190-112-16-11
<u>After Three Days</u>					
Free Water	No	Trace	No	1% ³	-
Setting	No	No	No	No	Trace
Re-Stirrable	Yes	Yes	Yes	Yes	Yes
Gelled	Yes	No	No	No	No
<u>After One Week</u>					
Free Water	No	-	-	-	-
Setting	No	-	-	-	-
Re-Stirrable	Yes	-	-	-	-
Gelled	Yes	-	-	-	-
<u>After Three Weeks</u>					
Free Water	No	4% ³	No	2% ³	3.6% ³
Setting	No	No	No	Yes ⁴	Yes
Re-Stirrable	Yes	Yes	Yes	No	No
Gelled	Yes	No	No	No	No
<u>After Six Weeks</u>					
Free Water	No	-	-	-	-
Setting	No	-	-	-	-
Re-Stirrable	Yes	-	-	-	-
Gelled	Yes	-	-	-	-

¹ copolymer of acrylamido-2-methylpropane sulfonic acid and N,N-dimethylacrylamide² density was calculated³ percent by volume⁴ settled silica was hard

[0030] From the test results set forth in the Table, it can be seen that Sample No. 1 did not develop free water and settling did not occur at any time during the 6 weeks of storage. Further, the suspension was gelled, but was re-stirrable to its original consistency. Sample No. 2 developed free water and was not gelled, but no settling occurred. Sample No. 2 was re-stirrable to its original consistency. Sample No. 3 did not develop free water, settling did not occur and it was not gelled. The suspension was stable for the 6 weeks it was monitored and did not require re-stirring before use. Sample No. 4 developed free water and settling occurred after 3 weeks. Sample No. 4 could be utilized by re-stirring after being stored for about 1 week. Sample No. 5 developed free water after 3 days and settling occurred thereafter. Sample No. 5 could also be used after storage for up to 1 week if re-stirred.

[0031] Thus, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those which are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit of this invention as defined by the appended claims.

Claims

1. A storable water-silica suspension for use in well cement compositions, which suspension comprises: water; silica; and a suspending agent selected from colloidal materials, clays and gel forming polymers.

2. A suspension according to claim 1, wherein said suspending agent is a colloidal material selected from carbon black, lignite, brown coal, humic acid, styrene-butadiene rubber latexes, polyvinyl alcohol latexes, acetate latexes, acrylate latexes, precipitated silica and pyrogenic silica, said colloidal material preferably being present in an amount of from 25% to 100% by weight of the water.

3. A suspension according to claim 1, wherein said suspending agent is a clay selected from bentonite, attapulgite, kalomite, meta kalomite, hectorite and sepiolite, said clay preferably being present in an amount of 0.5 to 8% by weight of the water.

4. A suspension according to claim 1, wherein said suspending agent is a polymer selected from copolymers of 2-acrylamido-2-methylpropane sulfonic acid and N,N-dimethylacrylamide, carragenan, scleroglucan, xanthan gum, guar gum, hydroxyethylcellulose, carboxymethylhydroxyethylcellulose, hydroxypropylguar, welan gum, acrylic acid copolymers and terpolymers and vinyl acetate copolymers and terpolymers, said polymer preferably being present in an amount of from 0.1% to 3% by weight of the water.

5. A suspension according to any of claims 1 to 4, wherein said suspending agent is present in said suspension in an amount of from 0.1% to 100% by weight of said water in said suspension.

6. A suspension according to any preceding claim wherein said water is fresh water or salt water.

7. A suspension according to any preceding claim wherein said silica is fine silica flour, silica flour, sand or any mixture of two or more thereof, and wherein the silica is preferably present in said suspension in an amount in the range of from about 50% to about 250% by weight of said water in said suspension.

8. A method of cementing a well bore, which method comprises combining a suspension as claimed in any of claims 1 to 7, with a cement composition comprising a hydraulic cement and water; introducing the mixture into a well bore; and allowing it to set.

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